SUMMARY

Enhancements in ballistic protective wear for soldiers rely heavily on the development of lightweight materials with increased moduli and strength. It is well established that an armors ballistic limit can be increased significantly by using materials with increased moduli and strength. The material modulus is important since the stress wave speed of the material is directly related to this property. Hence, the greater the moduli, the greater the volume of material involved in resisting projectile penetration.

The development of high performance fibers from flexible chain polymers has been a subject of intense interest over the past 30 years. This is due to the fact that many polymers have high theoretical moduli (in some cases greater than 200 GPa) and strengths. However, these properties have not been realized in commercial or laboratory conditions except in a few unique cases. The inability of commercial fibers to realize their full potential is limited, in large part, to our inability to process them into highly extended chain conformations.

In this STIR research program we investigated the potential of applying a process using subcritical and supercritical CO2 on selected commercially available fibers with the aim to significantly enhance key physical and mechanical properties. The process involves solid-state drawing the fibers in the CO2 medium to produce fibers with potentially greater extended chain conformations and crystallinities, which in turn, leads to fibers with greater stiffnesses and strengths. The results in this area has suggest that many of the salient benefits realized by drawing fibers in a conventional solvent or produced by hydrostatic solid-state extrusion are synergistically realized when drawing a polymer in subcritical or supercritical CO2. Although CO2 is a poor solvent for many polymers, we have shown that under certain conditions it may be ideal for effectively plasticizing the amorphous phase of many semi-crystalline polymers, thereby enhancing chain mobility during drawing. Further, unlike conventional liquid solvents, the high permeability of CO2 in many polymers allows for rapid and effective solvent (CO2) swelling, and extraction without damaging the fiber morphology. This, in turn, translates to fiber morphologies with fewer defects and higher degrees of crystallinity. Finally, when the CO2 is introduced as a non-solvent (e.g., by altering the temperature/pressure) hydrostatic pressure can be superimposed on the drawing stresses to suppress fiber failure during drawing and mimicking the stress states that are achieved in solid-state, hydrostatic extrusion.

The studies conducted under this ARO STIR Research Grant has shown that post-treatment in subcritical and/or supercritical CO2 significantly increase the moduli and strength of commercial ultrahigh molecular weight polyethylene (UHMWPE, Dyneema) and Nylon6,6 fibers. In the case of the Nylon6,6 fibers a >30% increase in strength and a >20% increase in modulus was realized. Similarly, for UHMWPE a >50% increase in modulus was realized and a >10% increase in strength was realized.

Note that once optimum process conditions are isolated, the research, although fundamentally important, may provide an environmentally benign approach to post-treating commercially available fibers with superior physical and mechanical properties. Also, since the research can utilize commercially available materials and moderate design of process equipment, scale-up to large quantities can be easily achieved in a few years. Thus, once the optimum process studies are completed, the technology could be readily implemented to significantly improve numerous soldier protection products within the next few years.

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13. ABSTRACT (Maximum 200 words)

Enhancements in ballistic protective wear for soldiers rely heavily on the development of lightweight materials with increased moduli and strength. It is well established that an armors ballistic limit can be increased significantly by using materials with increased moduli and strength. The development of high performance fibers from flexible chain polymers has been a subject of intense interest over the past 30 years. However, to date the mechanical properties of commercial fibers are far below their theoretical values. This is due in large part to our inability to process the materials to achieve highly crystalline structures from highly extended chain conformations. In this STIR research program the feasibility of using subcritical and supercritical CO2 in the processing of fibers with superior mechanical properties was investigated. The synergistic effects of CO2 as both a pressurizing medium as well as a reversible plasticizer was shown to dramatically improve the mechanical stiffness and strength of both nylon6,6 and ultrahigh molecular weight polyethylene. In the case of Nylon6,6 fibers a greater than 30% increase in stiffness along with a 20% increase in strength was realized. Similarly, post treatment on UHMWPE fibers (Dyneema) showed an increase in modulus of greater than 50% of the commercial fibers. In both cases, the CO2 treatment primarily increased the overall degree of crystallinity compared to air drawn fibers.

It should be noted that, although the research has strong fundamental interests, it provides an environmentally benign approach to process fibers with superior mechanical properties. Once additional studies are conducted to isolate optimum process ranges, scale-up should be relatively quick since the polymeric materials and process equipment are all commercially available.

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SYNOPSIS OF RESEARCH

Many militarily important products rely on the continual development of polymeric fibers with enhanced mechanical properties. The ballistic performance of personnel protective body armor can be significantly enhanced if both the fiber modulus and tenacity are increased. In addition, tire chord in military vehicles, clothing, mobile housing, rope, etc. can all be made stronger and/or lighter if the properties of the fibers used to make these materials can be enhanced.

The initial research investigates the feasibility of using an environmentally benign process on commercially available polymers to produce fibers with superior mechanical properties. Also, it is envisioned that this process could be readily scaled-up and implemented in any number of applications over a relatively short period of time. It is also envisioned that this technology would improve many civilian products as well.

Project Objectives

The objective of the research was to assess the feasibility of producing fibers with superior mechanical properties through solid-state drawing in the presence of subcritical and supercritical CO2. The strategy was to highly extended chain conformations in flexible chain polymers by promoting their ultradrawability through the use of CO2 as a process media. Once the highly extended conformations were realized, the process conditions were altered to promote crystallization.

This required both single and multi-stage drawing, whereby the experiments were conducted in the CO2 while in a gaseous, liquid, or supercritical state. It is anticipated that altering the CO2 state together with other process parameters (e.g., pressure, temperature, rate of draw, etc.) will promote new and unique process conditions for drawing this class of materials.

Relevant Prior Art

Tensile drawing of polyethylene (PE) [1-6] and several other semicrystalline polymers, such as isotactic polypropylene (iPP) [7-13], poly(oxymethylene) (POM) [14-16] or poly(tetrafluoroethylene) (PTFE) [17], to draw ratios of greater than 20 ("ultradrawing"), up to several hundred, produces fibers with excellent mechanical properties [18,19]. Consequently, the drawability of many commercially available polymers has been investigated, in particular by Porter et al., Ward et al., and Kanamoto et al. [16, 18, 20-26]. The ultimate properties of the fibers have been shown to vary greatly depending on the process method, chemical structure, and physical characteristics of the polymer and in all cases, the ultimate strengths are far from theoretical expectations [27]. Despite serious efforts, no ultrastrong fibers have been produced from nylons [28-31], syndiotactic polypropylene (sPP) [20,33] or semicrystalline poly(ethylene terephthalate) (PET) [22,34].

A number of models have been proposed for polymer drawing. Classic models focus on the transformation from a spherulitic to a fibrous morphology at small draw ratios and low temperatures [35,36]. It has been proposed that (ultra)drawability requires sliding of microfibrils [35,37], or local melting [38, 39]. Discussions of ultradrawability have also focussed on low levels of entanglements [40-42], on intermolecular forces [44], on crystal-crystal transformations [45], on crystal slip [46-48], or on structural characteristics of the polymer which affect the crystalline α-relaxation [49,50].

It is generally accepted that to attain maximum uniaxial draw, two conditions must be met. The chains must be translated through the crystal and the entanglements in the amorphous phase must be reduced [18]. The concentration of entanglements may be reduced in a number of ways by starting from a gel state, a mat of single crystals, or a reactor powder synthesized at low temperatures.

Solid state coextrusion (SSCE), developed by Porter [18], has been one of the most successful techniques for obtaining highly oriented polymers. In this technique the polymer is forced while in its solid state through a capillary die through the action of high compressive forces. The combined action of large hydrostatic compressive stress and shear stress produce highly oriented, chain extended crystal morphologies. This occurs, in large part, because microdefects are suppressed and annealed away as opposed to activated thereby promoting failure as happens in uniaxial tensile drawing.

A recent variation of the SSCE and conventional tensile drawing processes was developed in Japan. In this process, the polymer is passed through a silicone oil pressurized medium while being drawn [51]. This process was applied to POM extrudates. Using this method, extrudates were clear compared to opaque for the control (no pressure) specimens showing that even moderate hydrostatic pressures suppress void formation. In addition, the rods showed higher tensile moduli, 42 GPa compared 34 GPa, and higher tensile strength, 2.0 GPa compared to 1.4 GPa.

Another process method that has gained a significant amount of attention has been solvent assisted drawing [21,28,31]. In this process, the polymer is exposed to a small amount of solvent prior to drawing. The solvent plasticizes the fiber along with creating an imperfect crystal structure in the fiber precursor. This allows the precursor to be subsequently drawn to higher draw ratios than attained otherwise. Literature reported values showing 20% increase in strength can be achieved using this approach. However, solvent removal can be difficult and has shown to produce defects in the fiber.

Results obtained in this STIR Program

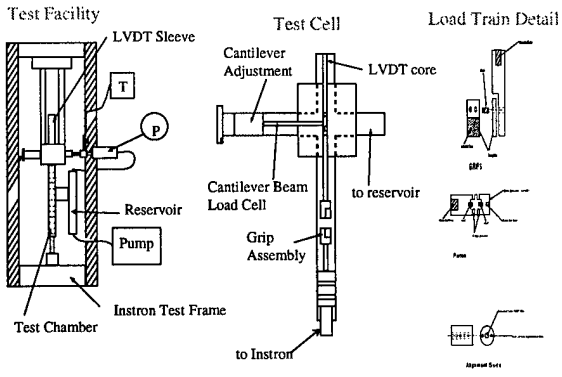
In this effort we investigated the concomitant effects of using CO2 as both a solvent for plasticizing the fiber and as a pressurizing medium. When CO2 is applied as a solvent we consider that many of the benefits reported with conventional solvent assisted drawing will be realized. Additionally, the relatively high diffusivity and permeability of CO2 in many polymers should provide for rapid swelling and solvent extraction without introducing microdefects into fiber as observed in conventional processes.

When CO2 is used as a nonsolvent at elevated pressures, we consider that many of the benefits realized with SSCE may be achieved by the CO2 acting to anneal defects and suppress premature failure during drawing. When CO2 is introduced as a poor solvent at elevated pressures (which is the most common condition for most polymers), then a hybrid of the two extreme conditions discussed above exist. We anticipate that drawing flexible chain polymers under these conditions synergistic effects might be realized that enable us to produce fibers with superior properties.

We envision that one unique feature that can produce a truly synergistic processing benefit is observed when CO2 is used in a "poor solvent state" on a semicrystalline polymer at moderate to high pressure and at temperature below the melt point. Previous work in our group has shown that, under these conditions, the CO2 will only penetrate into the amorphous phase and will be excluded from the crystal phase [52]. This causes the CO2 pressure to act uniformly over the entire crystal surface thereby more thoroughly and effectively removing defects from the crystalline phase during drawing.

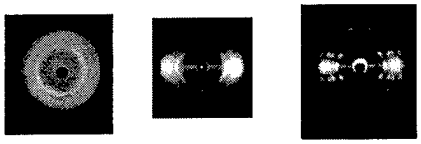
Our group has built an apparatus that allows us to conduct drawing experiments in CO2 mediated environments (see Figure 1). This apparatus is capable of drawing yarns and monofilaments while maintaining the pressure and temperature constant within the test cell. Additionally we measure in situ the draw stress on the filament using a designed leaf spring force transducer. The apparatus is mounted in an Instron 1333 tensile test machine which supplies the necessary reaction for the cell, controls the strain rate, and accurately measures the overall strain through crosshead movements.

Figure 1: Schematic of test cell and facility for solid-state drawing of fibers and films in high pressure CO2 mediated environments.



Recently we have used this facility to conduct single-stage drawing experiments on melt spun PET under subcritical and supercritical CO2 mediated environments [53]. Our results indicated that under certain conditions PET could be drawn to 30% higher draw ratios when compared to melt spun fibers treated with traditional solvents. Under a two-stage drawing process, the overall degree of crystallinity was moderately increased (11%) and the crystal quality was improved in certain conditions (see X-ray diffraction patterns in Figure2). This together with a measured increase in the amorphous orientation resulted in fibers with a 15% increase in modulus and 10% increase in tensile strength compared to conventional post-drawn processes.

Fig 2: WAXD patterns illustrating crystallinity development in PET fibers



Undrawn	**Stage One**	**Stage Two**
TDR = 1	TDR = 4	TDR = 12
CO_2 (105 atm)	CO_2(105 atm)	Air
23 °C	23 °C	200 °C

Post-treatment drawing studies were also conducted on Nylon6,6 tire chord obtained from Solutia Chemical Company. In this study all fibers were preconditioned in a 50% relative humidity environment prior to drawing. Drawing studies over a range of temperatures indicated that at a particular temperature range, the degree of crystallinity significantly increased and a moderate increase in the amorphous orientation was measured (see Figure 3). This translated into significant increases in both the modulus and strength (22% and 32% respectively) over that of fibers drawn in air mediated environments (see Figure 4).

Fig 3: Plots of degree of crystallinity (left) and amorphous orientation (right).

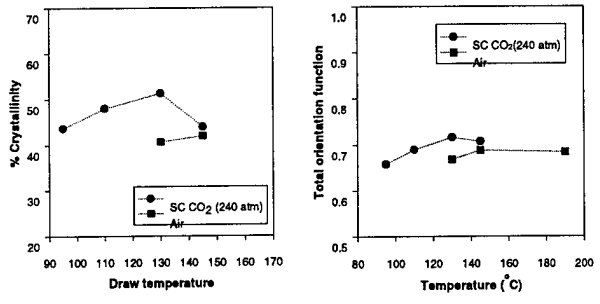
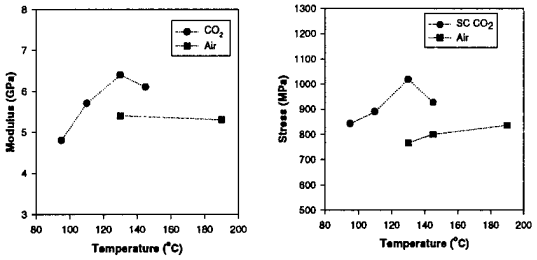
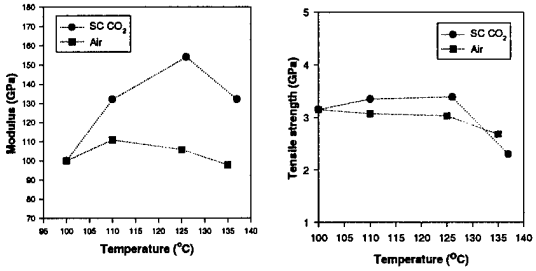


Fig 4: Plots of Nylon6,6 fiber modulus (left) and strength (right) for fibers drawn in CO2 mediated and air mediated environments



Similar effects were monitored in UHMWPE (Dyneema) fibers (see Figure 5.) Treatment with supercritical CO2 produced a pronounced 50% increase in modulus and 10% increase in fiber strength.

Fig 5: Plots of UHMWPE fiber modulus (left) and strength (right) for fibers drawn in CO2 mediated and air mediated environments



Although further studies are ongoing to elucidate the fundamental effects that the subcritical and supercritical CO2 has on both the amorphous and crystalline states of various polymeric materials, recent studies clearly illustrate the potential for employing this process method to develop fibers with superior properties.

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